High-efficiency capacitance performance from foam-like MnO_2/polyaniline/carbon nanotube film hybrids

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Abstract: Flexible supercapacitor electrode materials based on carbon nanotube film have been successfully fabricated. Honey-like MnO_2/polyaniline/Carbon nanotube film hybrids (MnO_2/PANI/CNTF) were manufactured via chemical oxidation polymerization and solution chemical reduction method. All electrochemical tests were carried out in a 1 M Na_2SO_4 electrolyte at a window voltage of -0.2-0.8 V. The structures and morphology of the hybrids are characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM). Raman spectroscopy and X-ray photoelectron spectrometer (XPS). The electrochemical performance was examined by cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD). MnO_2/PANI/CNTF hybrids exhibit a specific capacitance of 186 F/g at a current density of 1 A/g, which is much higher than of pure CNTF (20 F/g). After 1000 cycles, the capacitance was reduced by only 9 % compare to 15 % for PANI/CNTF hybrids and 19% for MnO_2 /CNTF.

Key words: carbon nanotube film; flexible; hybrids; PANI; MnO_2; supercapacitor

1. Introduction

Supercapacitors, also known as electrical double-layer capacitors, have drew much attention for its high power density, long operating life and fast charge-discharge process. On the basis of different action principles, supercapacitors are mainly made up of three major categories: double layer supercapacitor, pseudo capacitors and hybrid supercapacitors. What matters for the properties of the supercapacitor is the electrode materials. The customary electrode materials of double layer supercapacitor are carbon materials (Such as activated carbon, carbon nanotubes, carbon-aerogels, graphene material, etc.), corresponding to transition metal oxides (Such as hydroxides, oxides, nitrides and carbides) and conductive polymers (Such as polythiophene, polyaniline, polypyrrole and their corresponding derivatives) for pseudo capacitors. Hybrid supercapacitors are always composed of two or more carbon materials and pseudo capacitor electrode materials. Along with the progress and development of society, the traditional hard and flat electronic devices cannot meet the needs of mankind. Wearable, folding, portable electronic devices are becoming more and more popular. There are as vital to high flexibility as good electrochemical performances for supercapacitors. Therefore, how to solve the energy storage problem of flexible electronic devices is also one of the important factors to realize the application of electronic devices to wearable devices. Carbon nanotube film is common flexible substrates. CNTF, with high conductivity, good mechanical strength and ideal elasticity, is an excellent substrate for flexible electrode material. However, the low specific surface area of carbon nanotube leads to its low capacitance and limits its application, so increasing the specific surface area of the material is the key to improve the specific capacitance. Nowadays, it is our goal to develop a material with high power density, good energy density, environmental friendliness and lowering cost. It means that the electrode materials have advantages of both carbon and pseudo capacitor materials. Pseudo capacitor material that produces rapid, highly reversible redox reactions during energy storage, which leads to the same problem as batteries-the poor stability of the cycle. Pseudo capacitance electrode materials, including excessive metal oxides and polymers, have been concerned. It is a promising method to combine pseudo-capacitance electrode materials with CNTF. Compared with conventional polymers, conductive polymers have a low band gap (1-3 eV), which can rapidly charge and discharge, and produce fast doping and dedoping reactions. PANI, a kind of conductive polymer, recently has drew much attention recently for its easy synthesis, low cost and good conductivity. Liu et al. has used electrochemical polymerizatin to prepare CNTF/CNT/PANI electrodes with a specific capacitance of 67.31 mF/cm^{-2} at 0.5 mA/cm^{-2} in PVA-H_3PO_4 gel electrolyte. Li et al. reported the RGO/MnO_2/PANI composite paper with a large specific capacitance of 636.5 F/g at 1.0 A/g in 1.0 M Na_2SO_4. Among the many active electrode materials for supercapacitors, metal oxides have many advantages, such as high specific capacitance, low cost, rich resources and green environment. Compared with conventional carbon materials, it can greatly increase the energy density of supercapacitors and improve the electrochemical stability of supercapacitors compared with conducting polymers. Two ruthenium oxide is a kind of typical pseudo capacitive materials. The specific capacitance of prepared RuO_2 supercapacitor can reach 600 F/g. But ruthenium is a precious metal, the use of the battery voltage range and the high cost limits its potential application as small electronic devices. In addition to RuO_2, excessive metal oxide-MnO_2, owing to its good capacitance characteristics, wide using voltage, low cost and environmentally friendly advantages, has become the good choice for supercapacitor electrode material. MnO_2 has a high theoretical specific capacitance as high as 1370 F/g. And too much research has been working on it. Alonso-Marroquin has been fabricated CFF/MnO_2 electrodes by hydrothermal method with a specific capacitance of 467 F/g at 1 A/g.

Here in, honey-like structure MnO_2 and PANI nanowires are successfully synthesised onto the surface of CNTF. The induction of MnO_2 really enhances the cyclic stability of MnO_2/PANI/CNTF as well as the specific capacitance. The MnO_2/PANI/CNTF hybrids possess a good capacitance of 186 F/g at 1 A/g. And MnO_2/PANI/CNTF hybrids also express excellent flexibility as CNTF. Folding and bending has almost no effect to its electrochemical characteristics.

2. Experiment

2.1. Preparation of hybrid electrodes

CNT film(CNTF), cutting into pieces of specific dimensions 10 mm×10 mm by mechanical scissor, was immersed into a 1:3 (V:V) mixture of HNO3 and H_2SO_4 for 24 h to functionalize the surface, and then CNTF was washed several times by deionized water to remove residual acid on carbon nanotubes until the PH was 7. Finally, the CNTF was dried at 60 °C for 6 h.

PANI/CNTF hybrids was fabricated via chemical oxidation polymerization. 1 ml aniline was added to 1 mol/L (50 ml) H_2SO_4 solution. 0.025 mol APS was dissolved in 50 ml deionized water. Then, APS solution was quickly introduced into H2SO4 solution (containing aniline). After stirring for 1 minute, CNTF was put into the mixed solution. 12 h later, the PANI/CNTF hybrid was washed and dried stand-by.

The preparation of MnO_2/PANI/CNTF (MnO_2/CNTF) hybrid was manufactured according to the following steps: first, 0.15 mol potassium permanganate and 0.05 mol manganese sulfate were respectively dispersed in 20 ml distilled water and heated to 80 °C by Water Bath pot. Furthermore, PANI/CNTF (CNTF) was respectively dip into $KMnO_4$ and MnSO4 solutions. Finally, the hybrid film was washed and dried at 60 °C for 12 h.

2.2. Characterizations and Electrochemical Measurement

The morphology and microstructure of the hybrids were investigated by SEM and TEM. XPS analysis was carried out to examine the chemical components. The structural features of the composite film were further characterized by Raman spectra. The electrochemical performance was examined by CV, GCD and EIS. All the texts were carried out in 1 mol Na2SO4 with an operating voltage from -0.2 V to 0.8 V. The electrochemical tests were carried in a conventional three-electrode electrochemical system at room temperature. The MnO_2/PANI/CNTF hybrids was used as the working electrode. A platinum net severed as the counter electrode, and SCE acted as the reference electrode.

3. Result and discussion

3.1. Microstructure characterization

Morphologies of pure CNTF, PANI/CNTF, MnO_2/CNTF and MnO_2/PANI/CNTF are investigated by SEM as shown in Figure 1. It can be seen from Figure 1a that the pure CNTF has a porous network with many tubes interweaved and twined with a diameter of about 20-70 nm and several μm in length. In Figure 1b, the morphology of the PANI nanowires is very uniform with countless holes. The morphology of PANI/CNTF appears as nanowires with rough surface and interweaved, forming a net morphology and good interstitial structure, which is conducive to the full infiltration of the electrolyte. But beyond that, the diameter of the nanowires is about 100 nm and the length is more than 1 μm. Figure 1c displays the SEM image of MnO_2/CNTF. The morphology of MnO_2/CNTF exhibits a foam-like structure with many pores. The diameter of the pores is about 100 nm. In figure 1d, nanometer spherical MnO_2 are stacked on the surface of PANI, forming a honeycomb-like nanostructures. This structure has a large specific surface area, which is helpful for ion transfer and shortens the diffusion path of ions. It can promote electron transfer and improve the electrochemical properties of materials.

3.2. XPS and Raman of MnO_2/PANI/CNTF

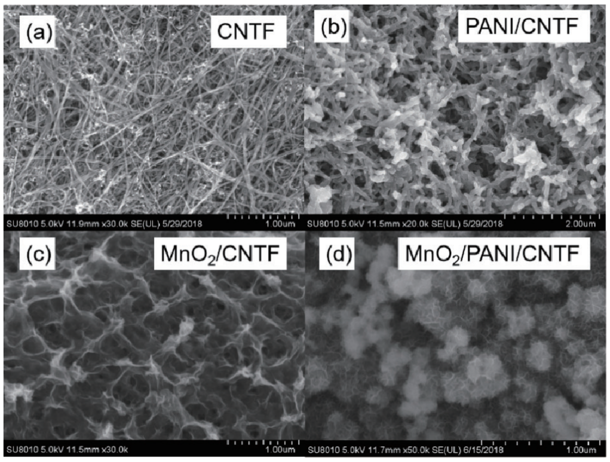

Figure 1. SEM images of the (a) pure CNTF (b) PANI/CNTF (c) MnO_2/CNTF (d) MnO_2/PANI/CNTF

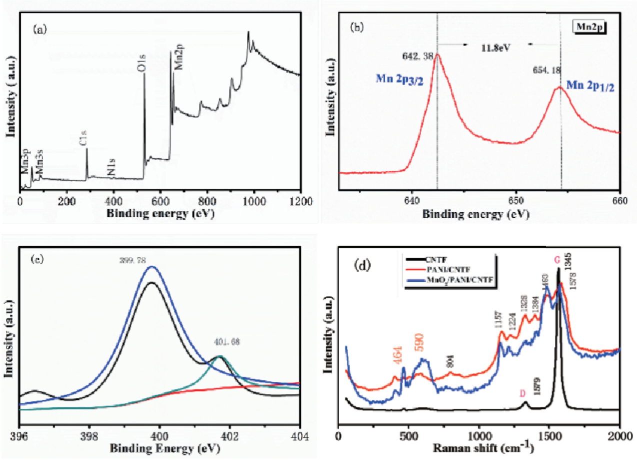

Figure 2.(a)XPS survey spectrum, (b) Mn 2p spectrum, (c) N 1s spectrum of the MnO_2/PANI/CNTF(d) Raman spectra of the pure CNTF, PANI/CNTF, MnO_2/PANI/CNTF.

XPS was carried out to better understand the chemical components and oxidation of Mn in the MnO_2/PANI/CNTF hybrids. The survey spectrum shows the peaks of Mn, C 1s, O 1s and N 1s. In figure2b, Mn 2p3/2 and Mn 2p1/2 is centered at 642.38 eV and 654.18 eV, respectively. The spin energy separation of 11.8 eV further demonstrates the existence of Mn4+ in MnO_2/PANI/CNTF. Figure 2c shows the XPS spectrum of N 1s. The binding energies located at 399.78 eV and 401.68 eV, respectively, belonging to-NH-and-NH+. XPS spectrum of N 1s illustrates that PANI is successfully synthesized on the surface of CNTF.

In order to obtain better confirmation on the presence of CNTF, PANI/CNTF, MnO_2/PANI/CNTF, raman spectroscopic investigation was also conducted. The structural features of the hybrid film are characterized by Raman analytical method in Figure 2d. It can be seen from figure 3 that two raman bands located at 1579 cm^{-1}, 1345 cm^{-1} are the characteristic peaks of CNTF: D peak and G peak. The peaks at 804 cm^{-1}, 1157 cm^{-1},1224 cm^{-1}, 1394 cm^{-1}, and 1483 cm^{-1} are the peaks of PANI compounds, indicating the formation of PANI nanowires in the hybrids. This is in good agreement with the result of XPS analysis. The D and G peaks of carbon nanotubes are also observed in PANI/CNTF, which is at 1328 cm^{-1} and 1578 cm^{-1}. The Raman spectra of MnO_2/PANI/CNTF is performed also. The peaks of PANI and CNTF can also be observed. The peak lying in 580 cm^{-1} and 454 cm^{-1} are the characteristic peaks of MnO_2, which indicates the presence of MnO_2 in MnO_2/PANI/CNTF hybrid.

3.3. Electrode materials characterization

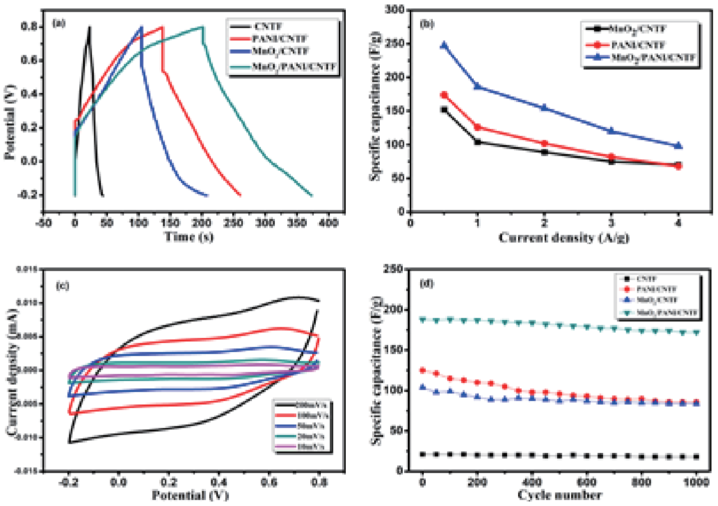

Figure 3.(a)Galvanostatic charge-discharge of CNTF, PANI/CNTF, MnO_2/CNTF and MnO_2/PANI/CNTF hybrids at 1 A/g. (b)Specific capacitance of PANI/CNTF, MnO_2/CNTF and MnO_2/PANI/CNTF from 0.5 A/g to 4 A/g. (c)The cycle voltammetrys of MnO_2/PANI/CNTF at different scanning rate. (d)Cycle performance of pure CNTF, PANI/CNTF, MnO_2/CNTF and MnO_2/PANI/CNTF hybrids at 1 A/g.

The electrochemical performances of prepared electrodes are exhibited in Figure 3. GCD and CV are investigated to characterize electrode chemical properties. The prepared electrode is tested with a nickel foam clip. All the testments are observed in a three-electrode system with a window voltage of -0.2~0.8 V. 1 mol/L Na_2SO_4 is used as an electrolyte. Figure 3a shows the GCD curves of the pure CNTF, PANI/CNTF, MnO_2/CNTF and MnO_2/PANI/CNTF hybrids at a current density of 1 A/g. The GCD curve of CNTF takes a shape of triangle, which indicates that the capacitance mainly comes from double layer. The specific capacitance of the pure CNTF, PANI/CNTF, MnO_2/CNTF and MnO_2/PANI/CNTF hybrids reach 21 F/g, 126 F/g, 103 F/g and 186 F/g, respectively. The charge-discharge curves of PANI/CNTF, MnO_2/CNTF and MnO_2/PANI/CNTF are not completely linear, which reflects faraday capacitance characteristics of hybrids. The charge-discharge performance of the PANI/CNTF, MnO_2/CNTF and MnO_2/PANI/CNTF hybrids are investigated at multiple current densities in figure 3b. When current density increases to 4 A/g, the specific capacitance reduces quickly. A highest specific capacitance of 247 F/g for MnO_2/PANI/CNTF is obtained at a current density of 0.5 A/g. The decay rate of the capacitance is 24.7 %, 17.3 %, 22.1 % and 19.4 %, as the current density increasing from 0.5 A/g to 4 A/g, which demonstrates that MnO_2/PANI/CNTF is suit for large current. The CVs of MnO_2/PANI/CNTF hybrid at different scanning rates are presented in Figure 3c. CVs of MnO_2/PANI/CNTF hybrid show quasi-rectangular shapes, indicating its good capacitive behavior. Figure 4d shows the cycle performance of CNTF, PANI/CNTF, MnO_2/CNTF and MnO_2/PANI/CNTF hybrids at the current density of 1 A/g. PANI/CNTF and MnO_2/CNTF display a higher specific capacitance compared to CNTF but a poor cyclic stability. The repeated doping and dedoping of PANI can cause the expansion and contraction of volume, which leads to damage of the chain skeleton of PANI and seriously reduce its cyclic stability. To compensate for poor stability, the honeycomb MnO_2 was compounded on the surface of PANI/CNTF. With the introduction of MnO_2, the capacitance is improved as well as the stability of the hybrids.

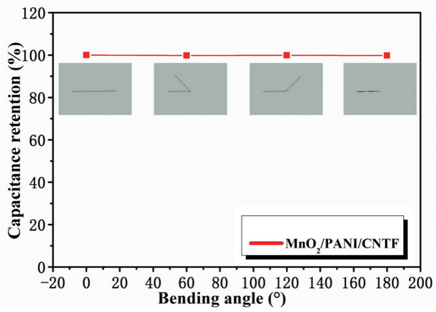

Figure 4.the capacitance retention of MnO_2/PANI/CNTF in different bending angle.

Folding and bending are typical characteristics of flexible supercapacitors. CNTF is an excellent flexible substrate. The flexible and capacitive properties of composite films are of vital importance. To verify the flexibility, MnO_2/PANI/CNTF held by nickel foam is folded from the middle to 0 °, 60 °,120 ° and 180 °. And then test its electrochemical properties. Figure 4a shows the capacitance retention of MnO_2/PANI/CNTF in different bending angle. The charge-discharge test is conducted at a current density of 1 A/g. Obviously, folding has almost no effect on its performance. This strongly indicates that MnO_2/PANI/CNTF film has great flexibility.

4. Conclusion

In summary, MnO_2/PANI/CNTF with a honey-like nanostructure has been successfully prepared by chemical oxidation polymerization and solution chemical reduction method. The hybrids show a highest specific capacitance of 247 F/g at a current density of 0.5 A/g and good cycle performance (91 % retention). The excellent capacitance characteristics is due to the porous structure, good mechanical and electrical contact and the facilitation of electron transport. As-prepared hybrid films reveal an excellent electrochemical properties and superb flexibility as flexible electrode. We believe that MnO_2/PANI/CNTF hybrid electrode is promising candidate for the application of flexible energy-storage supercapacitor.

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